

## Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters

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### Abstract

Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an “alternative” diesel fuel that is becoming accepted in a steadily growing number of countries around the world. Since the source of biodiesel varies with the location and other sources such as recycled oils are continuously gaining interest, it is important to possess data on how the various fatty acid profiles of the different sources can influence biodiesel fuel properties. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. In turn, the properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity.

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**Keywords:** Biodiesel; Branched fatty esters; Cetane number; Cloud point; Heat of combustion; Ignition delay time; Ignition quality tester; Low-temperature properties; Lubricity; Oxidative stability; Pour point; Straight-chain fatty esters; Viscosity

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## 1. Introduction

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats [1,2]. The transesterification of an oil or fat with a monohydric alcohol, in most cases methanol, yields the corresponding mono-alkyl esters, which are defined as biodiesel. The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are ASTM D6751 (ASTM=American Society for Testing and Materials) and the European standard EN 14214, which was developed from previously existing standards in individual European countries.

While the suitability of any material as fuel, including biodiesel, can be influenced by contaminants arising from production or other sources, the nature of the fuel components ultimately determines the fuel properties. Some of the properties included as specifications in standards can be traced to the structure of the fatty esters comprising biodiesel. However, as biodiesel consists of fatty acids esters, not only the structure of the fatty acids but also that of the ester moiety derived from the alcohol can influence the fuel properties of biodiesel. Since the transesterification reaction of an oil or fat leads to a biodiesel fuel corresponding in its fatty acid profiles with that of the parent oil or fat, biodiesel is a mixture of fatty esters with each ester component contributing to the properties of the fuel.

The properties of a biodiesel fuel that are determined by the structure of its component fatty esters include ignition quality, heat of combustion, cold flow, oxidative stability, viscosity and lubricity. The present work discusses the influence of the structure of fatty esters on these properties. Not all of these properties have been included as specifications in biodiesel standards, although all of them are essential to the proper functioning of the fuel.

## 2. Experimental

Cetane numbers (CN) of branched and straight-chain esters were determined in the Ignition Quality Tester™ (IQT™) described previously [3]. The IQT™ was calibrated with hexadecane and 2,2,4,4,6,8,8-heptamethylnonane (HMN) as primary reference fuels. CNs obtained with the IQT™ will be referred to as CN<sub>IQT</sub> in the text. This method has also become an ASTM standard test method (ASTM D6890), in which the CNs are termed derived cetane number (DCN).

For oxidation studies, an oxidative stability instrument apparatus was used to give oil stability index values with variations to AOCS (American Oil Chemists' Society) method Cd 12b-92 [4]. Kinematic viscosities were determined at 40 °C according to the standard test method ASTM D445 [5].

## 3. Results and discussion

Generally, methanol has been mostly used to produce biodiesel as it is the least expensive alcohol. Biodiesel in most cases can therefore be termed the fatty acid methyl esters (FAME) of a vegetable oil or animal fat. However, as mentioned above, both

moieties, the fatty acid chain and the alcohol functionality, contribute to the overall properties of a fatty ester and it is worthwhile to consider the properties imparted by other alcohols (yielding fatty acid alkyl esters; FAAE) that could be used for producing biodiesel. Therefore, both structural moieties will be discussed in the present paper. Table 1 lists fuel properties of neat alkyl esters of fatty acids.

### 3.1. Cetane number

As indicator of ignition quality, the CN is a prime indicator of fuel quality in the realm of diesel engines. It is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low CN and vice versa. The CN of a diesel fuel (DF) is related to the ignition delay (ID) time, i.e., the time that passes between injection of the fuel into the cylinder and onset of ignition. The shorter the ID time, the higher the CN and vice versa.

Standards have been established worldwide for cetane number determination, for example ASTM D613 in the United States, internationally the International Organization for Standardization (ISO) standard ISO 5165. A long straight-chain hydrocarbon, hexadecane ( $C_{16}H_{34}$ ; trivial name cetane, giving the cetane scale its name) is the high quality standard on the cetane scale with an assigned CN of 100. A highly branched compound, 2,2,4,4,6,8,8,-heptamethylnonane (HMN, also  $C_{16}H_{34}$ ), a compound with poor ignition quality, is the low-quality standard and has an assigned CN of 15. The two reference compounds on the cetane scale show that CN decreases with decreasing chain length and increasing branching. Aromatic compounds, which occur in significant amounts in conventional DF, especially DF2, have low CNs but their CNs increase with increasing size of *n*-alkyl side chains [6–8]. The cetane scale is arbitrary and compounds with  $CN > 100$  or  $CN < 15$  have been identified. The standard ASTM D975 for conventional DF requires a minimum CN of 40 while the standards for biodiesel prescribe a minimum of 47 (ASTM D6751) or 51 (EN14214). Due to the high CNs of many fatty compounds, which can exceed the cetane scale, the term lipid combustion quality number for these compounds was suggested [9].

For conventional diesel fuel, higher CNs have been correlated with reduced nitrogen oxides ( $NO_x$ ) exhaust emissions [10]. This correlation has led to efforts to improve the cetane number of biodiesel fuels by means of additives known as cetane improvers [11]. Despite the inherently relatively high CNs of fatty compounds,  $NO_x$  exhaust emissions usually increase slightly when operating a diesel engine on biodiesel. The connection between structure of fatty esters and exhaust emissions was investigated [12] by studying the exhaust emissions caused by enriched fatty acid alkyl esters as fuel.  $NO_x$  exhaust emissions reportedly increase with increasing unsaturation and decreasing chain length, which can also lead to a connection with the CNs of these compounds. Particulate emissions, on the other hand, were hardly influenced by the aforementioned structural factors. The relationship between the CN and engine emissions is complicated by many factors including the technology level of the engine. Older, lower injection pressure engines are generally very sensitive to CN, with increased CN causing significant reductions in the  $NO_x$  emissions due to shorter ignition delay times and the resulting lower average combustion temperatures. More

Table 1  
Properties of fatty acids and esters of relevance to biodiesel

Trivial (systematic) name; acronym <sup>a</sup>	m.p. <sup>b</sup> (°C)	b.p. <sup>b</sup> (°C)	Cetane number	Viscosity <sup>c</sup>	HG <sup>d</sup> (kg cal/mol)
Caprylic (octanoic); 8:0	16.5	239.3			
Methyl ester		193	33.6 (98.6) <sup>c</sup>	0.99 <sup>f</sup> ; 1.19 <sup>g</sup> ; 1.16 <sup>h</sup>	1313
Ethyl ester	−43.1	208.5		1.37 (25°) <sup>f</sup>	1465
Capric (decanoic); 10:0	31.5	270	47.6 (98.0) <sup>c</sup>		1453.07 (25°)
Methyl ester		224	47.2 (98.1) <sup>c</sup>	1.40 <sup>f</sup> ; 1.72 <sup>g</sup> ; 1.69 <sup>h</sup>	1625
Ethyl ester	−20	243–5	51.2 (99.4) <sup>c</sup>	1.99 (25°) <sup>f</sup>	1780
Lauric (dodecanoic); 12:0	44	131 <sup>1</sup>			1763.25 (25°)
Methyl ester	5	266 <sup>766</sup>	61.4 (99.1) <sup>c</sup>	1.95 <sup>f</sup> ; 2.43 <sup>g</sup> ; 2.38 <sup>h</sup>	1940
Ethyl ester	−1.8 <sup>fr</sup>	163 <sup>25</sup>		2.88 <sup>f</sup>	2098
Myristic (tetradecanoic); 14:0	58	250.5 <sup>100</sup>			2073.91 (25°)
Methyl ester	18.5	295 <sup>751</sup>	66.2 (96.5) <sup>c</sup>	2.69 <sup>f</sup> ; 3.23 <sup>h</sup>	2254
Ethyl ester	12.3	295	66.9 (99.3) <sup>c</sup>		2406
Palmitic (hexadecanoic); 16:0	63	350			2384.76 (25°)
Methyl ester	30.5	415–8 <sup>747</sup>	74.5 (93.6) <sup>c</sup>	3.60 <sup>h</sup> ; 4.38 <sup>g</sup> ; 4.32 <sup>h</sup>	2550
Ethyl ester	19.3/24	191 <sup>10</sup>	85.9 <sup>i</sup>		2717
Propyl ester	20.4	190 <sup>12</sup>	93.1 <sup>i</sup>		
<i>Iso</i> -propyl ester	13–4	160 <sup>2</sup>	85.0 <sup>i</sup>		
Butyl ester	16.9		82.6 <sup>i</sup>		
2-Butyl ester			91.9 <sup>i</sup>		
<i>Iso</i> -butyl ester	22.5	199 <sup>5</sup>	84.8 <sup>i</sup>		
	28.9		83.6 <sup>i</sup>		
Stearic (octadecanoic); 18:0	71	360 <sup>d</sup>	61.7 <sup>j</sup>		2696.12 (25°)
Methyl ester	39	442–3 <sup>747</sup>	86.9 (92.1) <sup>c</sup> ; 101 <sup>i</sup>	4.74 <sup>f</sup> ; 5.51 <sup>h</sup>	2859
Ethyl ester	31–33.4	199 <sup>10</sup>	76.8 <sup>i</sup> ; 97.7 <sup>i</sup>		3012
Propyl ester			69.9 <sup>i</sup> ; 90.9 <sup>i</sup>		
<i>Iso</i> -propyl ester			96.5 <sup>i</sup>		
Butyl ester	27.5	343	80.1 <sup>i</sup> ; 92.5 <sup>i</sup>		
2-Butyl ester			97.5 <sup>i</sup>		
<i>Iso</i> -butyl ester			99.3 <sup>i</sup>		
Palmitoleic (9(Z)- hexadecenoic); 16:1					
Methyl ester			51.0 <sup>i</sup>		2521
Oleic (9(Z)- octadecenoic); 18:1	16	286 <sup>100</sup>	46.1 <sup>j</sup>		2657.4 (25°)
Methyl ester	−20	218.5 <sup>20</sup>	55 <sup>j</sup> ; 59.3 <sup>i</sup>	3.73 <sup>f</sup> ; 4.51 <sup>g</sup> ; 4.45 <sup>h</sup>	2828
Ethyl ester		216–7 <sup>151</sup>	53.9 <sup>j</sup> ; 67.8 <sup>i</sup>	5.50 (25°) <sup>f</sup>	
Propyl ester			55.7 <sup>j</sup> ; 58.8 <sup>i</sup>		
<i>Iso</i> -propyl ester			86.6 <sup>i</sup>		
Butyl ester			59.8 <sup>j</sup> ; 61.6 <sup>i</sup>		
2-Butyl ester			71.9 <sup>j</sup>		
<i>Iso</i> -butyl ester			59.6 <sup>i</sup>		

Table 1 (continued)

Trivial (systematic) name; acronym <sup>a</sup>	m.p. <sup>b</sup> (°C)	b.p. <sup>b</sup> (°C)	Cetane number	Viscosity <sup>c</sup>	HG <sup>d</sup> (kg cal/mol)
Linoleic (9Z,12Z- octadecadienoic); 18:2	−5	229–30 <sup>16</sup>	31.4 <sup>j</sup>		
Methyl ester	−35	215 <sup>20</sup>	42.2 <sup>j</sup> ; 38.2 <sup>i</sup>		
Ethyl ester		270–5 <sup>180</sup>	37.1 <sup>j</sup> ; 39.6 <sup>i</sup>	3.05 <sup>f</sup> ; 3.65 <sup>g</sup> ; 3.64 <sup>h</sup>	2794
Propyl ester			40.6 <sup>j</sup> ; 44.0 <sup>i</sup>		
Butyl ester			41.6 <sup>j</sup> ; 53.5 <sup>i</sup>		
Linolenic (9Z,12Z,15Z- octadecatrienoic); 18:3	−11	230–2 <sup>17</sup>	20.4 <sup>j</sup>		
Methyl ester					
Ethyl ester	−57/−52	109 <sup>0.018</sup>	20.6 <sup>c</sup> ; 22.7 <sup>j</sup>	2.65 <sup>f</sup> ; 3.14 <sup>g</sup> ; 3.27 <sup>h</sup>	2750
Propyl ester		174 <sup>2.5</sup>	26.7 <sup>j</sup>		
Butyl ester			26.8 <sup>j</sup>		
Erucic (13Z-docosenoic); 22:1	33–4	265 <sup>15</sup>			
Methyl ester		221–2 <sup>5</sup>		5.91 <sup>f</sup> ; 7.21 <sup>h</sup>	3454
Ethyl ester		229–30 <sup>5</sup>			

<sup>a</sup> The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for 18 carbons and one double bond.

<sup>b</sup> Melting point and boiling point data from Refs. [64] and [65]; superscripts for boiling point data denote pressure (mm Hg) at which the boiling point was determined.

<sup>c</sup> Viscosity values determined at 40 °C unless indicated otherwise. See footnotes f, g or h if dynamic or kinematic viscosity data were reported.

<sup>d</sup> Heat of combustion values from Refs. [24] and [64].

<sup>e</sup> Number in parentheses indicates purity (%) of the material used for CN determinations as given in Ref. [19].

<sup>f</sup> Dynamic viscosity (mPa s=cP), Ref. [45].

<sup>g</sup> Kinematic viscosity (mm<sup>2</sup>/s=cSt), Ref. [5].

<sup>h</sup> Kinematic viscosity, Ref. [47].

<sup>i</sup> Ref. [3].

<sup>j</sup> Ref. [11].

modern engines that are equipped with injection systems that control the rate of injection are not very sensitive to CN [13–15].

Historically, the first CN tests were carried out on palm oil ethyl esters [16,17], which had a high CN, a result confirmed by later studies on many other vegetable oil-based diesel fuels and individual fatty compounds. The influence of compound structure on CNs of fatty compounds was discussed in more recent literature [18] with the predictions made in that paper being confirmed by practical cetane tests [3,9,11,19]. CNs of neat fatty compounds are presented in Table 1. In summary, the results are that CNs decrease with increasing unsaturation and increase with increasing chain length, i.e., uninterrupted CH<sub>2</sub> moieties. However, branched esters derived from alcohols such as *iso*-propanol have CNs competitive with methyl or other straight-chain alkyl esters [3,20]. Thus, one long, straight chain suffices to impart a high cetane number even if the other moiety is branched. Branched esters are of interest because they exhibit improved low-temperature properties.

Recently, cetane studies on fatty compounds were conducted using the IQT<sup>TM</sup> [3]. The IQT<sup>TM</sup> is a further, automated development of a constant volume combustion apparatus (CVCA) [21,22]. The CVCA was originally developed for determining cetane numbers more rapidly, with greater experimental ease, better reproducibility, reduced use of fuel and therefore less cost than the ASTM test method D613 utilizing a cetane engine. The IQT<sup>TM</sup> method, which is the basis of ASTM D6890, was shown to be reproducible and the results competitive with those derived from ASTM D613. Some results from the IQT<sup>TM</sup> are included in Table 1. For the IQT<sup>TM</sup>, ignition delay (ID) and cetane number are related by the following equation [3].

$$\text{CN}_{\text{IQT}} = 83.99 \times (\text{ID} - 1.512)^{-0.658} + 3.547 \quad (1)$$

In the recently approved method ASTM D6890, which is based on this technology, only ignition delay times of 3.6–5.5 ms (corresponding to 55.3 to 40.5 DCN) are covered as it is stated that precision may be affected outside that range. However, the results for fatty compounds with the IQT<sup>TM</sup> are comparable to those obtained by other methods [3]. Generally, the results of cetane testing for compounds with lower CNs, such as the more unsaturated fatty compounds, show better agreement over the various related literature references than the results for compounds with higher CNs. The reason is the non-linear relationship (see Eq. (1)) between the ignition delay time and the CN. The non-linear relationship between the ignition delay time and the CN was observed previously [23]. Thus, small changes at shorter ignition delay times result in greater changes in cetane number than at longer ignition delay times. This would indicate a leveling-off effect on emissions such as NO<sub>x</sub> as discussed above once a certain ignition delay time with corresponding CN has been reached as the formation of certain species depend on the ignition delay time. However, for newer engines, this aspect must be modified as discussed above.

The cetane scale also clarifies why fatty acid alkyl esters are suitable as diesel fuel. The reason is the long hydrocarbon chain in these esters and straight-chain alkanes, such as hexadecane, which have high cetane numbers.

### 3.2. Heat of combustion

Gross heat of combustion (HG) is another fuel property indicating the suitability of fatty compounds as diesel fuel. The heats of combustion of fatty esters and triacylglycerols [24,25] are in the range of approximately 1300 kg cal/mol to about 3500 kg cal/mol for C8–C22 fatty acids and esters (see Table 1). HG increases with chain length. Fatty alcohols possess heats of combustion in the same range [26]. The literature value [25] for the heat of combustion of hexadecane is 2559.1 kg cal/mol (at 20 °C). This value is in the same range as those of fatty compounds.

### 3.3. Cold flow properties

One of the major problems associated with the use of biodiesel is poor low-temperature flow properties, indicated by relatively high cloud points (CP) and pour

points (PP) [1,2]. The CP, which usually occurs at a higher temperature than the PP, is the temperature at which a liquid fatty material becomes cloudy due to formation of crystals and solidification of saturates. Solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems. With decreasing temperature, more solids form and the material approaches the pour point, the lowest temperature at which it will still flow. Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds (Table 1) and in a mixture they crystallize at higher temperature than the unsaturates. Thus biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher CPs and PPs.

Besides CP (ASTM D2500) and PP (ASTM D97), two test methods for the low-temperature flow properties of conventional DF exist, namely the low-temperature flow test (LTFT) used in North America (ASTM D4539) and cold filter plugging point (CFPP) used mainly outside North America (European standard EN 116). These methods have also been used to evaluate biodiesel and its blends with Nos. 1 and 2 conventional DF. Low-temperature filterability tests were stated to be necessary because of better correlation with operability tests than CP or PP [27]. However, for fuel formulations containing at least 10 vol.% methyl esters, both LTFT and CFPP are linear functions of CP [28]. Additional statistical analysis showed a strong 1:1 correlation between LTFT and CP [28].

Specifications related to low-temperature properties are included in biodiesel standards. Cloud point is the related property in ASTM D6751 but a limit is not given, rather a report is required. This is due to the strongly varying weather conditions in the United States. CFPP is discussed in EN14214. Each country can select one of two options (moderate or arctic climate) for seasonal classes (summer and winter) and modify this specification based on national meteorological data.

Several approaches to the low-temperature problems of esters have been investigated including blending with conventional DF, winterization, additives, branched-chain esters, and bulky substituents in the chain. The latter approach may be considered a variation of the additive approach as the corresponding compounds have been investigated in biodiesel at additive levels. Blending of esters with conventional diesel fuel will not be discussed here.

Numerous, usually polymeric, additives were synthesized and reported mainly in the patent literature to have the effect of lowering PP or sometimes even CP. A brief overview of such additives has been presented [2]. Relatedly, the use of fatty compound-derived materials with bulky moieties in the chain [29] at additive levels was investigated. The idea associated with these materials is that the bulky moieties in these additives would destroy the harmony of the crystallizing solids. The effect of some additives appears to be limited because they more strongly affect the PP than the CP or they had only slight influence on CP. The CP, however, is more important than the PP for improving low-temperature flow properties [30].

The use of branched esters such as *iso*-propyl, *iso*-butyl and 2-butyl instead of the methyl esters [31,32] is another approach for improving the low-temperature properties of biodiesel. Branched esters have lower melting points in the neat form (Table 1). These esters showed a lower  $T_{CO}$  (crystallization onset temperature) as determined by differential scanning calorimetry (DSC) for the isopropyl esters of soybean oil by 7–11 °C and for the 2-butyl esters of SBO by 12–14 °C [31]. The CPs and PPs were also lowered by the



branched-chain esters. For example, the cloud point of *iso*-propyl soyate was given as  $-9^{\circ}\text{C}$  [19] and that of 2-butyl soyate as  $-12^{\circ}\text{C}$  [31]. In comparison, the cloud point of methyl soyate is  $0^{\circ}\text{C}$  [28]. However, in terms of economics only *iso*-propyl esters appear attractive as branched-chain ester although they are more expensive than methyl esters. Branching in the ester chain does not have any negative effect on the CNs of these compounds as discussed above.

Winterization [30,33,34] of vegetable oil esters is based on the lower melting points of unsaturated fatty compounds versus saturated compounds (Table 1). This method removes by filtration the solids formed during cooling of the vegetable oil esters, leaving a mixture with higher content of unsaturated fatty esters and thus with lower CP and PP. This procedure can be repeated to further reduce the CPs and PPs. Saturated fatty compounds, which have higher CNs (Table 1), are among the major compounds removed by winterization. Thus the CN of biodiesel decreases during winterization. Loss of material was reduced when winterization was carried out in presence of cold-flow improvers or solvents such as hexane and *iso*-propanol [34].

In other work [35], tertiary fatty amines and amides were reported to be effective in enhancing the ignition quality of biodiesel without negatively affecting the low-temperature properties. Also, saturated fatty alcohols of chain lengths  $> \text{C}_{12}$  increased the PP substantially. Ethyl laurate weakly decreased the PP.

### 3.4. Oxidative stability

Oxidative stability of biodiesel has been the subject of considerable research [4,36–45]. This issue affects biodiesel primarily during extended storage. The influence of parameters such as presence of air, heat, light, traces of metal, antioxidants, peroxides as well as nature of the storage container was investigated in the aforementioned studies. Generally, factors such as presence of air, elevated temperatures or presence of metals facilitate oxidation. Studies performed with the automated oil stability index (OSI) method confirmed the catalyzing effect of metals on oxidation with copper showing the strongest catalyzing effect; however, the influence of compound structure of the fatty esters, especially unsaturation as discussed below, was even greater [4]. Numerous other methods, including wet-chemical ones such as acid value and peroxide value, pressurized differential scanning calorimetry, etc., have been applied in oxidation studies of biodiesel.

The reason for autoxidation is the presence of double bonds in the chains of many fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds [46]. The positions allylic to double bonds are especially susceptible to oxidation. The *bis*-allylic positions in common polyunsaturated fatty acids such as linoleic acid (double bonds at  $\Delta 9$  and  $\Delta 12$ , giving one *bis*-allylic position at C-11) and linolenic acid (double bonds at  $\Delta 9$ ,  $\Delta 12$ , and  $\Delta 15$ , giving two *bis*-allylic positions at C-11 and C-14), are even more prone to autoxidation than allylic positions. Relative rates of oxidation given in the literature [46] are 1 for oleates (methyl, ethyl esters), 41 for linoleates, and 98 for linolenates. This is essential because most biodiesel fuels contain significant amounts of esters of oleic, linoleic or linolenic acids, which influence the oxidative stability of the



fuels. The species formed during the oxidation process cause the fuel to eventually deteriorate. Small amounts of more highly unsaturated fatty compounds had a disproportionately strong effect [4].

A European standard (pr EN 14112) has been established for potential inclusion of an oxidative stability parameter in the European biodiesel standard EN 14214. The biodiesel standard EN 14214 calls for determining oxidative stability at 110 °C with a minimum induction time of 6 h by the Rancimat method. The Rancimat method is nearly identical to the OSI method, which is an AOCS (American Oil Chemists' Society) method. The ASTM standard D6751 currently does not include any specification of this kind.

### 3.5. Viscosity

Viscosity affects the atomization of a fuel upon injection into the combustion chamber and thereby ultimately the formation of engine deposits. The higher the viscosity, the greater the tendency of the fuel to cause such problems. The viscosity of a transesterified oil, i.e., biodiesel, is about an order of magnitude lower than that of the parent oil [1,2]. High viscosity is the major fuel property why neat vegetable oils have been largely abandoned as alternative diesel fuel. Kinematic viscosity has been included in biodiesel standards (1.9–6.0 mm<sup>2</sup>/s in ASTM D6751 and 3.5–5.0 mm<sup>2</sup>/s in EN 14214). It can be determined by standards such as ASTM D445 or ISO 3104. Values for kinematic viscosity of numerous fatty acid methyl esters have been reported [47].

The difference in viscosity between the parent oil and the alkyl ester derivatives can be used to monitor biodiesel production [48]. The effect on viscosity of blending biodiesel and conventional petroleum-derived diesel fuel was also investigated [49] and an equation was derived which allows calculating the viscosity of such blends.

The prediction of viscosity of fatty materials has received considerable attention in the literature. Viscosity values of biodiesel/fatty ester mixtures were predicted from the viscosities of the individual components by a logarithmic equation for dynamic viscosity [50]. Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. This holds also for the alcohol moiety as the viscosity of ethyl esters is slightly higher than that of methyl esters. Factors such as double bond configuration influence viscosity (*cis* double bond configuration giving a lower viscosity than *trans*) while double bond position affects viscosity less [5]. Branching in the ester moiety, however, has little or no influence on viscosity [5], again showing that this is a technically promising approach for improving low-temperature properties without significantly affecting other fuel properties. Values for dynamic viscosity and kinematic viscosity of neat fatty acid alkyl esters are included in Table 1.

### 3.6. Lubricity

With the advent of low-sulfur petroleum-based diesel fuels, the issue of diesel fuel lubricity is becoming increasingly important. Desulfurization of conventional, petroleum-derived diesel fuel reduces or eliminates the inherent lubricity of this fuel, which is essential for proper functioning of vital engine components such as fuel pumps and injectors. However, non-sulfur polar compounds are also eliminated from petrodiesel during the

desulfurization process and it is likely the loss of these compounds and not the sulfur-containing materials that causes the loss of lubricity [51]. Another study states that phenols and polyaromatic compounds are the species imparting lubricity to petrodiesel fuels [52].

Several studies [53–63] on the lubricity of biodiesel or fatty compounds have shown the beneficial effect of these materials on the lubricity of conventional petroleum-derived diesel fuel, particularly low-sulfur petrodiesel fuel. Adding biodiesel at low levels (1–2%) restores the lubricity to low-sulfur petroleum-derived diesel fuel. An advantage of biodiesel compared to lubricity-enhancing additives is that biodiesel inherently possesses fuel properties competitive and compatible with conventional petroleum-based diesel fuel, which those additives usually do not possess. No significant effects of biodiesel fatty acid composition on lubricity were reported, except for castor oil which displayed better lubricity than other vegetable oil esters [53]. Unsaturated acids exhibited better lubricity than saturated species [62]. Ethyl esters had improved lubricity compared to methyl esters [53]. Fatty acids possess excellent lubricating properties [60]. Standards for testing the lubricity of diesel fuels use the scuffing load ball-on-cylinder lubricity evaluator (SLBOCLE; ASTM D6078) or the high-frequency reciprocating rig (HFRR; ASTM D6079; ISO 12156). Lubricity has not been included as specification in biodiesel standards despite the definite advantage of biodiesel versus petrodiesel with respect to this fuel property.

#### 4. Summary and conclusions

The above discussion shows that the fuel properties of biodiesel are strongly influenced by the properties of the individual fatty esters in biodiesel. Both moieties, the fatty acid and alcohol, can have considerable influence on fuel properties such as cetane number with relation to combustion and exhaust emissions, cold flow, oxidative stability, viscosity, and lubricity. Generally, cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. It therefore appears reasonable to enrich (a) certain fatty ester(s) with desirable properties in the fuel in order to improve the properties of the whole fuel. For example, from the presently available data it appears that *iso*-propyl esters have better fuel properties than methyl esters. The major disadvantage is the higher price of *iso*-propanol in comparison to methanol, besides modifications needed for the transesterification reaction. Similar observations likely hold for the fatty acid moiety. It may be possible in the future to improve the properties of biodiesel by means of genetic engineering of the parent oils, which could eventually lead to a fuel enriched with (a) certain fatty acid(s), possibly oleic acid, that exhibits a combination of improved fuel properties.

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